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Modeling the Response of Fluid/Melt Explosives to Slow Cook-off

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Abstract. To understand the violence of fluid/melting explosives subject to an external heat source, it is necessary to understand the thermal-mechanical-chemical-flow response of the explosive. We build on our previous success in modeling the thermal and mechanical response in solid explosives by making changes to the ALE3D coupled physics code to handle reacting explosive fluids. Beginning with a single velocity incompressible flow model, we added handling the composition, defining composition dependent material properties, chemical buoyancy effects, coupling to the solid container, and transition to short time scale calculations. We describe the model and demonstrate how it affects the Comp-B ODTX experiment.

Introduction

It is important to understand the conditions under which energetic materials undergo spontaneous reaction, and their ensuing violence. With this understanding, one can design mitigation strategies that reduce the probability of spontaneous reaction while the system is subject to adverse environments, and reduce the consequences of that reaction.

One important adverse environment is fire, where the energetic material may be subject to a thermal ignition event leading to a thermal explosion. For solid explosives the process of heat transfer is simply conductive, and can be modeled with a simple thermal/chemical code, as the explosive does not move significantly during the heating process. In the past few years we have developed more extensive models for solid

explosives which include not only the thermal transport process but also the mechanical response¹², porosity and surface tension³ in the explosive, and improved chemical reaction networks⁴. With this level of detail we have been able to successfully model the thermal mechanical response of HMX based explosives undergoing a thermal build up to explosion. However, liquid explosives or those that melt early in the heat up phase are much more complicated, as they require a different treatment of material motion effects. The explosive can no longer be treated using an implicit mechanical assumption, but must make assumptions that define the flow of the material. This flow changes the way the energy and composition are moved around the system, as those characteristics are now moved with the material itself in a convective manner, as well as the original diffusive processes.

In this paper, we describe the changes that were made to ALE3D⁵ to model fluid and melting explosives. The overall goal of this modeling effort is to predict the violence of the explosive reaction. This means that one needs to be able to continuously model the explosive from the initial relatively quiescent pre-ignition phase to the much more violent post-ignition phase. Doing this requires that all physical processes need to be modeled during all phases of the calculation, though not necessarily with the same set of approximations. Much as we did with solid explosives, where we model the system using an implicit mechanics scheme and then transition to an explicit mechanics scheme to handle the final reaction phase, we look to construct a model that couples slow mechanical and fluid processes during the pre-ignition phase and then transitions to an explicit final phase. These changes included adding models for chemically reacting fluids, modeling the fluid interaction with its solid confinement, and the transition between slow and fast physics.

We take these improvements and demonstrate their use on the One Dimensional Time to eXplosion (ODTX) on Comp-B. This explosive is a melt cast explosive mixture of RDX and TNT.

Modeling Liquid Explosives

In order to model liquid explosives in ALE3D, we started with an incompressible flow model that had been developed to model simple fluid flows.

Incompressible Flow Model

The incompressible flow model in ALE3D is based on a semi-implicit pressure projection method⁶. The governing equations for the incompressible, variable viscosity model are

$$\rho_0 \left(\frac{\partial u}{\partial t} + u \cdot \nabla u \right) = -\nabla p + \nabla \cdot \mu (\nabla u + (\nabla u)^T) + g\rho$$

$$\nabla \cdot u = 0$$

where ρ_0 is the reference density, μ is time and space varying molecular viscosity, u is the flow velocity, and p is the dynamic pressure. The incompressibility assumption removes the need for a sound speed courant condition in the solution,

but does require an implicit pressure and velocity solve. The momentum/velocity field is solved with a second order accurate finite element method resulting in a non-divergence free intermediate velocity. A projection step is then applied where a Poisson equation for the pressure correction is solved for and the solution used to project the intermediate velocity to a divergence free solution. For robustness with strongly varying viscosity, the viscous terms are treated with a first order accurate backward Euler time integration. The convective terms are treated explicitly.

Species Advection/Diffusion

Traditionally materials and their state have been handled as element centered variables in the hydrodynamic portion of the code. In the incompressible flow model, these are handled as node centered variables. The process of updating the concentrations is split between an advection/diffusion and a reaction step. The advection/diffusion step uses an explicit forward Euler advection component and implicit backward Euler diffusion scheme. A single iteration is taken each time step, thereby requiring that the time step be limited by a courant condition based on the fluid velocity. The reaction step uses the same chemical reaction framework used in the rest of the code, but uses the nodal temperature and average pressure to compute the reaction rates based on the user defined set of reaction mechanisms.

Composition Dependent Properties

The fluid properties of viscosity, thermal diffusivity, and species diffusivity are computed from the full state of the system. For multi-species materials, the properties for each species are computed using the current state, and then averaged. For viscosity, a volumetric weighted geometric averaging scheme:

$$\ln(\mu) = \sum_s v_s \ln(\mu_s)$$

Where μ , μ_s , and v_s are the mixed viscosity, species viscosity, and species volume fraction respectively.

The species diffusion constant is computed using a mass weighted harmonic averaging scheme:

$$\frac{1}{D_s} = \sum_j \frac{x_j}{D_{sj}}$$

Where D_s , D_{sj} , and x_j are the effective species diffusion constant, the s-j pair diffusion constant, and the species j mass fraction, respectively.

The thermal conductivity λ is computed using a volume harmonic average from the species conductivity λ_s :

$$\frac{1}{\lambda} = \sum_s \frac{v_s}{\lambda_s}$$

Boussinesq Buoyancy Approximation

It is typical in an incompressible flow model to treat buoyancy effects with a Boussinesq approximation. In such an approach, the density variations are small enough to be ignored for the inertial terms, but gravity induced specific weight is not negligible. Typically, one would simply apply a simple volume expansion coefficient. For our purposes, we forgo the simple expansion coefficient for a more complex effective density computation. We define a complete equation of state for the fluid material, and then use the reference pressure and the current temperature to compute an effective density that is used for the buoyancy computation. All equations of state in ALE3D are defined in terms of relative volume v and energy e . Non-(e,v) states are determined by iterating on the (e,v) guess using a Newton solver until the a relative pressure/temperature error of 10^{-6} is obtained.

When the fluid material model supports chemical reactions, as is the case with an explosive, this process of computing the effective density from the equation of state naturally handles the species density variation. This chemical composition Boussinesq approximation can then be used to drive not only temperature driven variations but also compositionally driven ones.

Incompressible Flow/Implicit Hydrodynamics Coupling

In order to predict explosive violence in these fluid systems, one must model the full system during the pre-ignition phase of the calculation, as this defines the state for the run up to reaction and violence. To do this it is necessary to have two types of models running simultaneously: an incompressible flow model for the fluid explosive, and an implicit hydrodynamics model for the solid components of the system.

The fluid to solid coupling is handled as a pressure boundary condition. This requires that the flow model provide a pressure that can be used in that boundary condition. We first determine the contiguous regions of fluid by doing a connectivity search through the mesh. This allows the user to define multiple discontinuous regions of the problem space with the same material parameters, each with their own average pressure. Then a pressure is computed on each node based on the current composition, temperature, and reference density. This pressure is volume averaged over the connected areas of the problem to compute an average pressure. This average pressure is combined with the flow pressure to define a pressure boundary condition for the implicit hydrodynamics step. Since the evolution of the system is expected to be slow, this boundary condition is applied explicitly in time.

Nominally, the total volume of the incompressible flow portion of the system is to remain fixed during the duration of the problem. However, if the fluid acts on the containing vessel, then that vessel would have to respond by changing its volume. Since we expect the volume change to be small, we accept the volume change in the solution, and depend on the divergence free projection operator to return us to a divergence free velocity field. Since the nodes are allowed to move during the calculation, it is necessary to reform the matrix during each solution step.

Transitioning between Incompressible Flow and Explicit Dynamics

As the explosive starts to react, the time step will begin to drop. At some point, that time step

will become small enough that the computational time to perform the larger incompressible flow and implicit hydro time steps is larger than the time to simply run the calculation with an explicit time step. The nominal fluid sound speed is computed using the underlying equation of state information. From this the explicit courant time step is obtained and used to compare with the current problem time step. The code automatically transitions from using the implicit methods to using the explicit mechanics scheme when the ratio of the explicit courant time step to the current time step is greater than 1%.

During that transition, several things need to be done to continue the computation. First, the compositional data needs to be moved from being a node centered quantity to an element centered one. This is accomplished by a simple average of the nodal values associated with each element. Next, the state of the fluid system needs to be recomputed to be consistent. This is done by making use of the average fluid pressure defined in the previous section. The new internal energy and relative volume are iteratively computed using the current zone averaged temperature, the compositional state, and the fluid average pressure.

During the run-up to the transition, it is not uncommon for the fluid velocity field to become chaotic. Because of this, although we could have transitioned the fluid velocity field to the new explicit velocity, we have chosen to zero that velocity instead. This is similar to what is done when we transition from the implicit mechanics solution to the explicit solution. In the latter case, the two velocity fields do have very little in common, as one is an average displacement field and the other an instantaneous velocity.

Because of all of the changes that the system goes through during the transition from an implicit solver to an explicit solution scheme, we cut the time step to a thousandth of the courant time step. This allows the system several time steps to equilibrate locally without wild gyrations in the macro scale.

Assuming that the fluid/solid interactions were handled properly during the long time scale model, the transition from long time scale models to short time scale models is the most important for predicting the overall violence of the event. The transition to the short time scale must be

smooth, otherwise the pressure transients can overwhelm the actual thermal variations in the problem, and could even induce ignition on their own.

Model for Comp-B ODTX Experiment

We use the framework of a Comp-B ODTX experiment to demonstrate the new reacting fluid capabilities in ALE3D.

Comp-B Model

An example of a fluid/melting explosive is Comp-B, which is a mixture of 39.4% TNT, 59.5% RDX and 1% wax by weight. We treat Comp-B as a chemical material with two species – a reactant and a product. A single temperature dependent viscosity⁷ is applied to the chemical material model, and is shown in Figure 1. The viscosity model contains two significant drops corresponding to the TNT and RDX melt temperatures. Both reactants and products use a simple equation of state:

$$P = 4.5 \text{ GPa} \left(\frac{\rho}{\rho_0} - 1 \right) + 0.01128 e$$

Where ρ is the density, ρ_0 is the reference density, and e is the energy per reference volume in GPa. The reactant has a reference density of 1.695, and the product that of 1. It was decided that using a significantly smaller reference density for the product species would not be consistent with operating in an incompressible flow framework. The heat capacity for both species is 1.13 J/gm K, and the heat released by the reaction is 1.2 Kcal/gm.

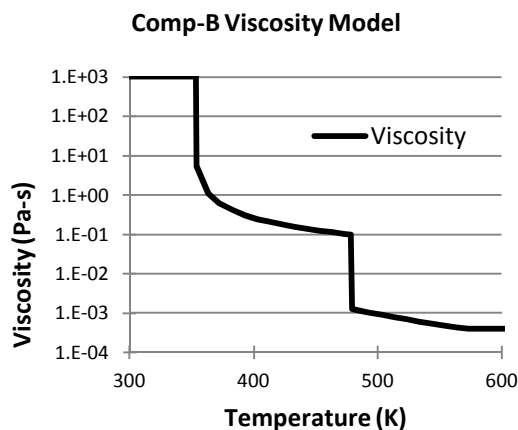


Fig. 1. Viscosity as a function of temperature for Comp-B. The two drops in viscosity are due to the melting of TNT and RDX, respectively.

A simple reaction model is used to transform between reactants and products:

$$\dot{x}_r = -x_r(x_p + 0.01x_r) \exp\left(51.961 - \frac{27233}{T}\right)$$

Where \dot{x}_r is the rate of change of the reactant in inverse seconds, x_r and x_p are the reactant and product mass fractions, respectively, and T is the temperature in Kelvin. These parameters were derived from DSC measurements and ODTX calculations assuming that the Comp-B remained a solid until it decomposed.

ODTX Model

A 2D-axisymmetric model of the ODTX was developed for these simulations. The mesh consisted of 12672 elements which were divided into 8 computational domains to allow the problem to be run in parallel on 8 processors. Of these elements, 3456 elements were associated with the explosive, and 9216 associated with the Aluminum anvil. The mesh was merged, so there are no slide surfaces between the explosive and the anvil.

The initial temperature for all parts was set to 293 K. In order to prevent thermal instabilities caused by a temperature jump, all external surfaces of the anvil were ramped to the set point temperature over 0.1 sec. The temperature on the outside of the anvil was then maintained at the set point until problem termination.

A point in the problem needs to be constrained from moving in the axial direction in order to remove the free translational degree of freedom from the implicit mechanics solution. We chose the point where the explosive and the anvil meet that has the largest distance from the axis of symmetry. Beyond removing the unwanted degree of freedom, this also forces the anvil to center on the explosive. This prevents significant mesh skewing as the anvil expands that would occur if one were to pick the point on the axis or worse, on the bottom of the anvil.

In order to drive the convective flow, a 1G gravitational acceleration is applied along the axial direction. The incompressible flow average pressure is applied as a boundary condition to the inside of the anvil.

In addition to modeling Comp-B as a molten explosive, it is useful to compare the system as if it were a solid. In order to do this, we turn off both the incompressible flow and implicit hydrodynamic models, treating the system as fixed in space.

Results

The Comp-B ODTX was simulated as both a

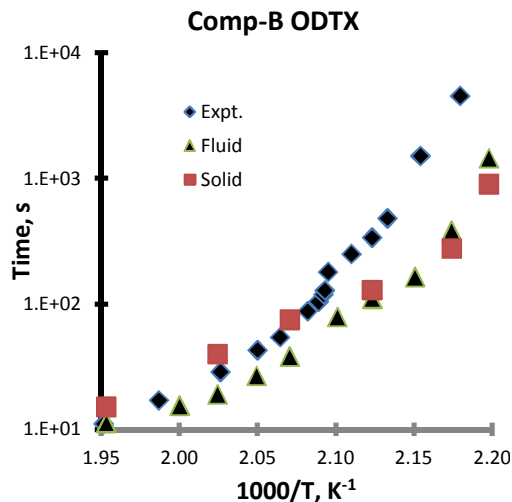


Fig. 2. Comparison between experimental, fluid model, and solid model for the time to thermal explosion of Comp-B as a function of inverse temperature.

fluid and a solid with several hold temperatures. The results are compared to experiment in Fig 2. It is interesting to note that, as expected, the times to explosion for the system treated as a solid gives reasonable agreement to experimental results where the model was calibrated. It is also interesting that the time to explosion modeled as a fluid is faster at high temperatures and slower at low temperatures than the equivalent solid model.

Let us now examine several states. Fig. 3 shows the flow pattern that is set up during the early stages of the simulation. At this early stage, the TNT on the outside of the explosive has melted, and being lighter than the colder solid, begins to flow up. The solid sinks and we start to form a pool of hot liquid at the top of the ODTX. This pattern brings hot and reacting material together earlier than in the absence of flow. This can lead to an enhanced reactivity as long as this flow pattern is maintained.

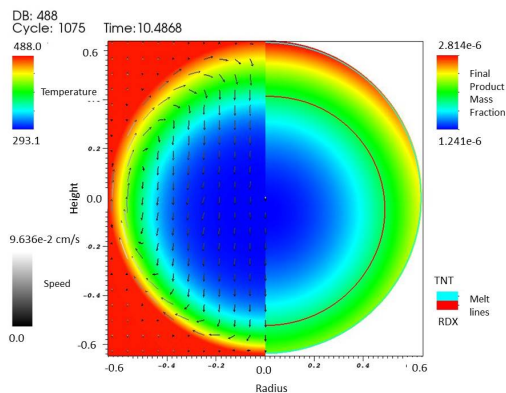


Fig 3. ODTX at hold temperature 488 after ~10.5 seconds. The left half of the figure is a temperature in K pseudo-color plot and a 1 second streamline of the flow. The right half of the figure is a mass fraction of the reaction products pseudo-color plot and the two melt temperature contours. This plot is typical of an early time state where the outside layer has melted, and the solid is settling down through the lower density fluid.

Depending on the external hold temperature, there are two flow patterns that form in late time. In Fig. 4, we show the high temperature flow pattern. Under these conditions, there are 3 distinct flow regions. Near the bottom, we continue to see the sinking of the higher density solid in the low density fluid. In the middle, where the fluid is still cooler than the anvil, we see a standard convective flow pattern, where the fluid near the hot surface rises and the fluid away from the surface sinks. Finally, near the top we see a different pattern. Here the explosive has become hot enough to start reacting. This reaction heats the fluid, causing it to rise. As the hot fluid nears the anvil, it cools off and tends to flow down. However, the reaction produces a lower density species whose buoyancy will counter the temperature gradient driven flow.

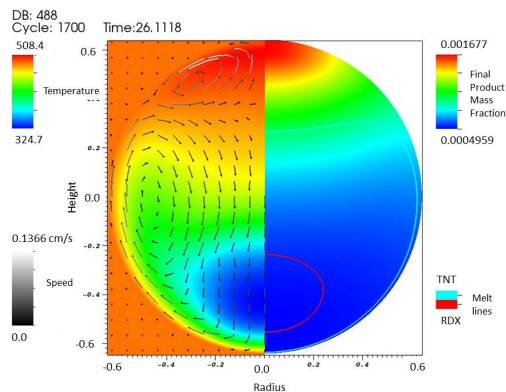


Fig. 4. ODTX at hold temperature 488 after ~26 seconds. Displaying the same items as Fig 3. Note the sinking solid, the standard convective flow in the low temperature fluid, and the reacting convective flow in the fully melted explosive.

For low temperature hold temperature, the entire explosive has a chance to melt. We show the late time pattern in Fig 5. Here the flow is completely generated by the heating from the decomposition. Note that the hottest material is flows to the top, where it is cooled by the anvil, and then slides to the bottom. This flow pattern in essence keeps the explosive cooler than it would be in the absence of flow, thus retarding the onset of ignition. The creation of a low viscosity bubble, as seen by the high temperature contour in Fig. 5 provided the space for a small recirculation zone

that helps maintain the integrity of the hot spot. It is also interesting to note that as the fluid equilibrates with the anvil, the flow direction changes. During that period, the inertia from the flow will actually drive the low density/high temperature/reaction region toward to bottom until the buoyancy overcomes the inertia and establishes the reverse flow.

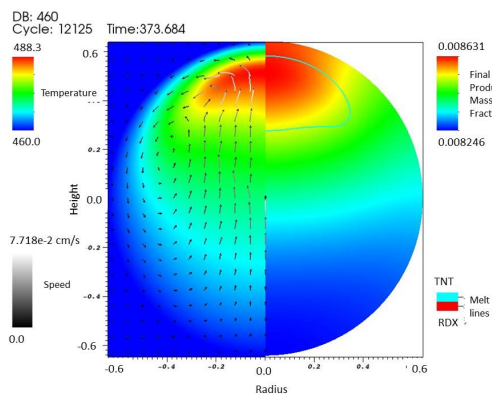


Fig. 5. ODTX at hold temperature 460 after ~ 374 seconds. Displaying the same items as Fig. 3. In this case, all of the TNT in explosive has melted, and the flow pattern is driven by the heat release from the explosive decomposition reaction.

As the explosive heats up, the rate of reaction increases to the point where the time step drops to where it is more efficient to run the calculation explicit. We show the pressure and relative volume after that transition and near thermal runaway in Fig. 6. There are no transition artifacts in the pressure which would have arisen if the pre- and post-transition explosive pressure were significantly different. Also note the location of the high pressure expanding gas near the top of the ODTX, associated with thermal ignition. In a solid explosive, the ignition would either be in the center or in a radial shell. This loss of symmetry is completely driven by the gravitational forces on the fluid.

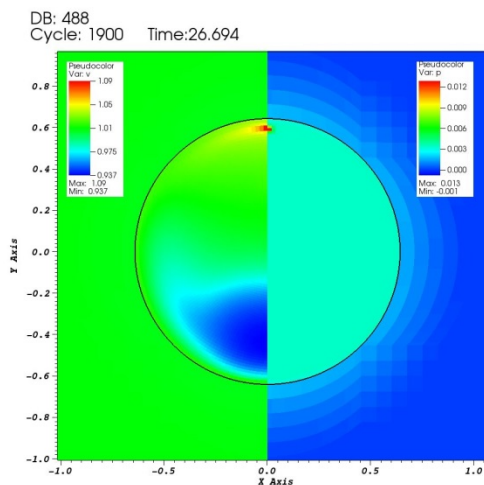


Fig. 6. The computed relative volume (left) and pressure in Mb (right) after the simulation transitioned from implicit to explicit solution schemes and shortly before thermal runaway. Note the high pressure and increased relative volume near the top where the system is starting to ignite.

Conclusions

In this paper we have described the changes that were made to ALE3D's incompressible flow model to create an initial capability for modeling fluid/melting explosives. These changes included adding support for species concentration on the fluid mesh, adding an effective equation of state for the fluid that could be used to provide buoyancy terms, composition dependent material properties, improved fluid/solid interactions, and a mechanism to transition the problem from implicit solution schemes to an explicit scheme. All of these capabilities were implemented in both 2- and 3- dimensions.

We have shown that with these modifications we can model fluid/melting explosives. In modeling the ODTX, we have seen several interesting features which arise from the self-heating of the explosive, where the explosive sets up its own flow patterns. We have also shown that we can smoothly transition from the implicit long time step solution schemes to the explicit short time step. This is a necessary step toward the prediction of violence, as this sets the initial state for the transition from the global decomposition

model to a deflagration model, which we have shown how to model previously.

There are several avenues of future development for this model. Currently all species move together with the same flow velocity. This implies that there is no gravity induced segregation which could be important, especially when gases should accumulate at the top of a device. The incompressible framework ignores the momentum change associated with change of state (heating, reacting). This is clearly a deficiency that needs to be addressed by going to a compressible implicit fluid solution scheme. Such schemes are currently being examined. One might also want to consider that the partially melted system might be better represented with a multi-velocity model, where the solid doesn't move because it is packed into the container, while the fluid moves between the solid particles.

Acknowledgements

The authors would like to thank the ALE3D team for providing the framework and support for the development of this model. The parameter set used for these calculations was provided by the early work of Dr. Matthew McClelland. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. The authors would like to acknowledge the Joint DoD / DOE Munitions Technology Development Program (JMP) for funding to perform this work.

References

1. A. L. Nichols III, R. Couch, R. C. McCallen, I. Otero, R. Sharp, "Modeling Thermally Driven Energetic Response of High Explosives", Proceedings of the 11th International Detonation Symposium, Snowmass, CO, Office of Naval Research, 1998, pp 862-871
2. A. L. Nichols III, A. Anderson, R. Neely, B. Wallin, "A Model for High Explosive Cookoff", Proceedings of the 12th International Detonation Symposium, San Diego, CA, Office of Naval Research, 2002, pp 94-102
3. Nichols, A. L. III, "Improving the Material Response for Slow Heat of Energetic Materials", Proceedings of the 14th International Detonation Symposium, Coeur d'Alene, ID, Office of Naval Research, 2010, pp 991-999
4. Nichols, A. L., III, "Improving the Model Fidelity for the Mechanical Response in a Thermal Cook-off of HMX", APS SCCM, Chicago, IL, 2011, AIP Conf Proc. 1426 551-554 (2012)
5. Nichols, A. L. III, Editor, "User's Manual for ALE3D, An Arbitrary Lagrange/Eulerian 2D and 3D Code System", Lawrence Livermore National Laboratory, LLNL-SM-650174, 2014..
6. Gresho, P. M and Sani, R. L. "On the theory of semi-implicit projection methods for viscous incompressible flow and its implementation via a finite element method that also introduces a nearly consistent mass matrix, Part 2: implementation", Intl. J. for Num. Methods in Fluids 11, pp.621-660, 1990.
7. Nunez, M. P., Zerkle, D. K. and Zucker J. M. "The rheology of molten Composition B" Los Alamos National Lab Report LA-UR-12-24029 (2012).

Question

Michael Hobbs, SNL

Your flow fields are a consequence of the Boussinesq flow assumption. Isn't the actual process a two-phase flow problem? Isn't bubbly flow a better assumption than Boussinesq flow? Your chemistry is too simple. Do you plan to include relevant processes such as RDX dissolution, suspension settling, etc.?

Reply by Dr. Nichols

For the types of problems that we are looking at, even bubble creation does not change the density significantly (we are assuming a gas tight system). Therefore, the assumption of density driven flow is a reasonable one. The chemical reaction framework in place is capable of handling an arbitrarily complex reaction mechanism. The current chemistry is indeed very simple, and we

expect to increase the complexity as we continue to develop our models. Factors like dissolution can easily be added within our reaction framework. We acknowledge that settling of RDX (segregation) is a limitation of our current model, and we are currently developing a framework to model the gravity driven segregation.